

Defects in Ethylene-Propylene Copolymer Crystals Drive Change in Lattice Geometry

W. Hu¹, S. Srinivas¹, and E.B. Sirota²

¹ExxonMobil Chemical Company; ²ExxonMobil Research and Engineering Company

By using x-ray light generated by the National Synchrotron Light Source, Exxon Mobil Corporation scientists have undertaken the challenging task of determining how defects affect the structure of crystals. Combining the power of wide-angle x-ray scattering and solid-state nuclear magnetic resonance, the scientists have shown how the incorporation of methyl branches in polyethylene crystals affect their transition from an orthorhombic to a hexagonal phase.

Defects exist in all crystalline materials and exert a substantial effect on their physical and mechanical properties. The structure of defects in large-molecule crystals, such as polymers, is highly complex. So, many experimental and theoretical investigations have been and are still being very actively pursued.

In polymer crystals, scientists distinguish two types of defects, called dynamic and static. Dynamic defects are thermally-activated, large-amplitude chain motions that facilitate the deformation and mechanical damping of the crystals, whereas static defects are mostly due to the non-regularity of monomer units along polymer chains.

One example of static defect is that in ethylene (C₂H₄) copolymers, especially ethylene-propylene (EP) copolymers. By copolymerizing ethylene and propylene (C₃H₆), the polymer chain has mostly (CH₂)_n units with randomly placed methyl (CH₃) side groups or branches. EP and other such "defected" polyethylenes, called linear low-density polyethylene (LLDPE), are of substantial commercial importance, with an annual U.S. production of more than 3.5 million tons.

With increasing defect concentration in the crystal, the crystalline lattice changes from an orthorhombic phase, with little or no methyl branches, to a hexagonal phase, with more methyl branches.

We studied the structure of static defects in EP copolymers at beamline X10A using wide-angle x-ray scattering (WAXS) and solid-state nuclear magnetic resonance (NMR), and found that chain motion in the crystal may serve as an important connection between the defect structure and change in the crystalline lattice.

WAXS data of a series of EP samples (**Figure 1**) show that the area per chain of the orthorhombic phase increases at increasing methyl branch content, and that the hexagonal phase emerges when the fraction of backbone carbons containing a methyl branch is larger than 0.095.

The hexagonal phase has an area per chain of 21Å², about 14 percent greater than that of the orthorhombic phase. The increased area in the hexagonal phase is probably due to a decrease in packing density caused by disorder and not merely due to lower density caused by packing of the branched chains. The abrupt change of area per chain upon the transition from an orthorhombic to a hexagonal phase indicates that the hexagonal phase is a distinct phase, rather than an inherently



Authors (from left): Srivatsan Srinivas, Weiguo Hu, and Eric B. Sirota

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Contact information

Weiguo Hu, ExxonMobil Chemical Company, Baytown, TX

Email: weiguo.hu@exxonmobil.com

orthorhombic phase with a hexagonal geometry.

Solid-state nuclear magnetic resonance (NMR) spectra of several EP samples (**Figure 2**) show that the isotropic chemical shift (ICS), which is the slight difference between the intrinsic frequency at which each sample resonates and the frequency imposed by the NMR apparatus, changes from 32.8 parts per million (orthorhombic phase) to 33.4 parts per million (typical of rotator phase) at increasing propylene content. This can be interpreted as an increase in rotational freedom at higher defect levels, which occurs simultaneously with the expansion of the crystalline lattice seen in **Figure 1**. In the rotator phase, each chain has approximate rotational symmetry, and thus the packing of the chains is naturally hexagonal. So, the rotator phase observed by NMR should be the hexagonal phase detected by WAXS.

Combining the observations from the two techniques, we propose the following picture that seems to connect the observations for defect, molecular motion, and lattice geometry. In the polyethylene crystals that do not contain methyl branches, the motion of the chains is a 180-degree flip, followed by a slip by half the distance of a repeat unit. In crystals containing methyl branches, pure flip becomes less favorable because local segments containing methyl branches do not have the flip-and-slip symmetry as an ethylene chain without methyl branches. As a result, a certain amount of rotation is added to the motional mode. Since this component gives chains more cylindrical symmetry, it causes the lattice change from orthorhombic toward hexagonal. Eventually, the increase in rotation amplitude leads to the transition to the rotator/hexagonal phase.

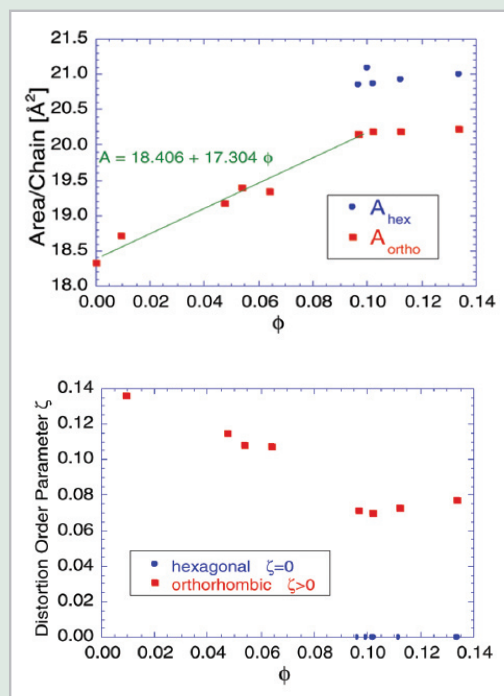


Figure 1. (Top) The computed area/chain, assuming the two peak orthorhombic structure (A_{ortho}) and single peak hexagonal phase (A_{hex}). (Bottom) The distortion order parameter, defined as a distortion away from hexagonal. ϕ is the fraction of backbone carbons containing a methyl (CH_3) branch.

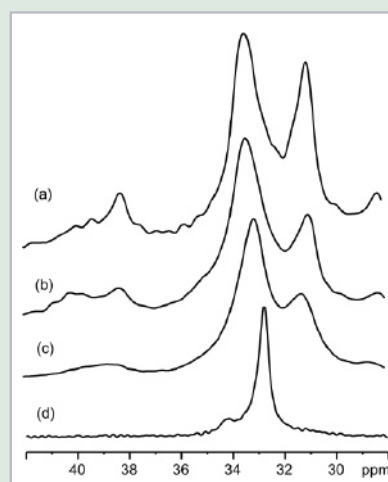


Figure 2. Cross polarization/magic angle spinning (CP/MAS) solid-state nuclear magnetic resonance spectra of ethylene-propylene copolymers for different values of ϕ , the fraction of backbone carbons containing a methyl (CH_3) branch: (a) 0.133, (b) 0.102, (c) 0.064, and (d) 0.